

Abstracts of Forthcoming Articles

Chalkogenides of the Transition Elements. X. X Ray, Neutron, Mössbauer and Magnetic Studies of Pentlandite and the π Phases $\pi(\text{Fe}, \text{Co}, \text{Ni}, \text{S}), \text{Co}_8\text{MS}_8$ and $\text{Fe}_4\text{Ni}_4\text{MS}_8$ ($M = \text{Ru}, \text{Rh}, \text{Pd}$). O. KNOP, C. H. HUANG, K. I. G. REID, AND J. S. CARLOW. Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada. AND F. W. D. WOODHAMS. Department of Natural Philosophy, University of Aberdeen, Aberdeen AB9 2UE, Scotland. The metal atoms in the cubic π phases (Fe, Co, Ni, M)₈S₈ occupy four-coordinated majority and six-coordinated minority sites in the ratio 8:1. X ray and neutron powder diffraction of Co₈MS₈ and Fe₄Ni₄MS₈ ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Ru}, \text{Pd}$) has shown that the structures are ordered, i.e., with M segregated in the minority sites, when M is a 4d element, and at best partially ordered when M is a 3d element. Magnetic susceptibility measurements and Mössbauer ⁵⁷Fe spectra show that Co₉S₈ and the natural $\pi(\text{Fe}, \text{Ni}, \text{S})$ phase, pentlandite, remain Pauli-paramagnetic down to 4.2°K, with no resultant magnetic moments on the metal atoms, and hence are broad-band metals. Linear dependence of the isomer shifts at the two types of sites in a variety of (Fe, Co, Ni)₈S₈ compositions indicates the existence of a composite s - d conduction band. Analysis of the variation of the quadrupole splitting at the majority site with composition leads to the conclusion that only a few levels at the bottom of the conduction band are occupied. The number of electrons in the band is approximately proportional to the total d -electron content of the unit cell. A tentative band scheme based on these results and on other available evidence is proposed. The effect of composition on the interatomic distances in the π phases is discussed.

Transition Metal Iodates. VII. Crystallographic and Nonlinear Optic Survey of the 4f-Iodates. S. C. ABRAHAMS, J. L. BERNSTEIN, AND K. NASSAU. Bell Laboratories, Murray Hill, New Jersey 07974. Thirteen crystallographically distinct families of 4f-iodates, including hydrates, have been investigated. The anhydrous Type I family, extending from Ce to Lu, crystallizes in the monoclinic system, space group $P2_1/a$: the lattice constants of Gd(IO₃)₃, for example, are $a = 13.389 \pm 0.006$, $b = 8.500 \pm 0.002$, $c = 7.106 \pm 0.002$ Å, $\beta = 99.73 \pm 0.03^\circ$, with four formulas per unit cell. Yb(IO₃)₃ and Lu(IO₃)₃ also crystallize in Type II with monoclinic space group $P2_1/c$ and lattice constants for Yb(IO₃)₃ of $a = 8.685 \pm 0.005$, $b = 6.066 \pm 0.002$, $c = 16.687 \pm 0.009$ Å, $\beta = 115.01 \pm 0.18^\circ$, and four formulas per unit cell. Polycrystalline samples only of the anhydrous Types III, IV, V, and VI have been prepared and typical powder patterns are given. All anhydrous 4f-iodates form in centrosymmetric space groups. La and Ce grow as hemihydrates in the orthorhombic space group $C222_1$, with $a = 19.26 \pm 0.01$, $b = 7.40 \pm 0.01$, $c = 6.76 \pm 0.01$ Å for La(IO₃)₃·½H₂O, and both generate second harmonics more efficiently than quartz. Ce, Pr, Nd, Pm, and Sm form monohydrates, space group $P2_1$, with lattice constants for Sm(IO₃)₃·H₂O of $a = 10.080 \pm 0.007$, $b = 6.642 \pm 0.006$, $c = 7.250 \pm 0.008$ Å, $\beta = 112.9 \pm 0.1^\circ$, and two formulas per unit cell. The monohydrates are also more efficient than quartz at generating second harmonics. Two dihydrated families grow: Type I from Tm to Lu and Type II from Nd to Er, both triclinic. (Lu(IO₃)₃·2H₂O has $a = 8.018 \pm 0.012$, $b = 9.956 \pm 0.021$, $c = 6.969 \pm 0.016$ Å, $\alpha = 99.8 \pm 0.2^\circ$, $\beta = 93.8 \pm 0.2^\circ$, $\gamma = 68.2 \pm 0.2^\circ$ with two formulas in the unit cell, space group $P\bar{1}$. Nd(IO₃)₃·2H₂O has $a = 7.56 \pm 0.04$, $b = 10.77 \pm 0.05$, $c = 7.34 \pm 0.02$ Å, $\alpha = 105.3 \pm 0.4$, $\beta = 110.8 \pm 0.7^\circ$, $\gamma = 97.9 \pm 0.6^\circ$, with two formulas per cell and space group $P\bar{1}$. Polycrystalline Gd to Lu(IO₃)₃·4H₂O, and Ce to Sm(IO₃)₃·5H₂O Type I form in centrosymmetric space groups; powder patterns for two tetrahydrates and the four pentahydrates are given. La(IO₃)₃·5H₂O and Pr(IO₃)₃·5H₂O, Type II, are monoclinic, space group $P2_1/m$, with lattice constants for Pr(IO₃)₃·5H₂O of $a = 6.768 \pm 0.008$, $b = 23.120 \pm 0.039$, $c = 7.107 \pm 0.007$ Å, $\beta = 112.7 \pm 0.1$, and four formulas per unit cell.

Thermodynamic Characterization of Ternary Compounds. I. The Case of Negligible Defect Association. D. M. SMYTH. Materials Research Center, Lehigh University, Bethlehem, Pennsylvania 18015. The complete thermodynamic specification of the state of a ternary compound requires control of one more experimental parameter than for the case of a binary compound. Two experimental approaches have been used: (a) equilibration with a fixed activity of one of the binary constituents of the ternary com-